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## **JAPANESE / ENGLISH TRANSLATION OF**

**Japanese Patent Application JP 2002 – 275217 A**

**Title: Ethylene- $\alpha$ -Olefin Copolymer for Modifying Biodegradable Resin, Composition Thereof, and Articles Molded Therefrom**

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(54) [Title of the Invention]

**Ethylene- $\alpha$ -Olefin Copolymer for  
Modifying Biodegradable Resin,  
Composition Thereof, and Articles Molded  
Therefrom**

(57) [Summary]

[Object] To provide an ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins that has excellent flexibility, extrudability, and calenderability, and generates little heat when the end product is incinerated.

**[Means of Achievement]** An ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins composed of ethylene and a C<sub>3</sub> to C<sub>12</sub>  $\alpha$ -olefin and satisfying the following conditions (a) through (d):

- (a) The  $\alpha$ -olefin content must be 5 to 95% by weight
- (b) Mooney viscosity: ML<sub>1+4</sub> 100°C must be 5 to 150
- (c) The tensile stress ML<sub>100</sub> measured according to JIS-K-6251 must be 8 MPa or less
- (d) The Q value (weight-average molecular chain length/number-average molecular chain length) measured by GPC must be four or higher

**[Claims]**

**[Claim 1]** An ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins composed of ethylene and a C<sub>3</sub> to C<sub>12</sub>  $\alpha$ -olefin and satisfying the following conditions (a) through (d):

- (a) The  $\alpha$ -olefin content must be 5 to 95% by weight
- (b) Mooney viscosity: ML<sub>1+4</sub> 100°C must be 5 to 150
- (c) The tensile stress ML<sub>100</sub> measured according to JIS-K-6251 must be 8 MPa or less
- (d) The Q value (weight-average molecular chain length/number-average molecular chain length) measured by GPC must be four or higher.

**[Claim 2]** The ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins of Claim 1 that satisfies conditions (a) through (d) of Claim 1 and (e) below.

- (e) The molecular weight distribution curve must exhibit two or more peaks

**[Claim 3]** A biodegradable resin composition that contains (A) and (B) hereunder, with the content of (A) being 5 to 95 parts by weight and the content of (B) being 5 to 95 parts by weight.

- (A) The ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins of Claim 1
- (B) Biodegradable resin

**[Claim 4]** A biodegradable resin composition wherein (B) of Claim 3 contains at least one or more types of components selected from among biodegradable resins based on starch, corn starch, microbes, succinic acid, polyester amides, polycaprolactones, cellulose acetates, and polylactic acid.

**[Claim 5]** An extrusion-molded article obtained by extrusion-molding the biodegradable resin composition of Claim 3.

**[Claim 6]** Hoses, tubes, gaskets, packings, sheets, and films obtained from the molded article of Claim 5.

**[Claim 7]** A calender-molded article obtained by calendar-molding the biodegradable resin composition of Claim 3.

**[Claim 8]** Sheets or films obtained from the molded article of Claim 7.

**[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]** The present invention relates to an ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins, a composition thereof, and articles molded therefrom. More specifically, the present invention relates to an ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins that exhibits excellent flexibility, extrudability, and calenderability when blended with a biodegradable resin, and reduces damage to incinerator furnaces because the end product generates minimal heat when incinerated; a biodegradable resin composition thereof; and extrusion-molded articles and calender-molded articles obtained by respectively extrusion-molding and calendar-molding the biodegradable resin composition.

**[0002]**

**[Prior Art]** Thermoplastic resins such as polyethylene, polypropylene, polystyrene, polyethylene terephthalate, and polyvinyl chloride are widely used packaging materials, containers for foodstuffs, sundry items, household electrical appliances, and other products. These products are discarded from the home or factory after use, and are ultimately disposed of in landfill or by being incinerated.

**[0003]** The amounts of such thermoplastic resins used over the past few years have sharply increased. This has accordingly caused a dramatic increase in the amounts discarded from homes and factories, with the lack of landfill space around cities and towns having become a serious problem. Such thermoplastic resins remain in the environment without breaking down after having been discarded, which leads to unsightly litter, contamination of the ecosystem of aquatic organisms, and other problems. This has created a significant social problem. On the other hand, when the thermoplastic resins are incinerated, the generation of noxious exhaust gases can be controlled by performing high-temperature incineration, but the heat of combustion generated by this method can shorten the life of the incineration furnace.

**[0004]** Attention has consequently turned toward biodegradable polymers over the past few years to resolve these problems. However, their low melt tension during molding endows them with

poor roll release properties in calendering and poor shape retention during extrusion, which has led to molding-related complications.

[0005]

**[Problems to Be Solved by the Invention]** With the foregoing aspects of the prior art in view, an object to be resolved by the present invention is to provide an ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins, a composition thereof, and articles molded therefrom, in order to obtain a biodegradable resin composition with excellent flexibility, extrudability, and calenderability that enables damage to incineration furnaces to be reduced because minimal heat is generated by the end product on incineration.

[0006]

**[Means Used to Solve the Above-Mentioned Problems]** Specifically, a first invention of the present invention relates to an ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins composed of ethylene and a  $C_3$  to  $C_{12}$   $\alpha$ -olefin and satisfying the following conditions (a) through (d):

- (a) The  $\alpha$ -olefin content must be 5 to 95% by weight
- (b) Mooney viscosity:  $ML_{1+4}$  100°C must be 5 to 150
- (c) The tensile stress  $ML_{100}$  measured according to JIS-K-6251 must be 8 MPa or less
- (d) The Q value (weight-average molecular chain length/number-average molecular chain length) measured by GPC must be four or higher.

A second invention of the present invention relates to a biodegradable resin composition obtained by compounding the above ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins with a biodegradable resin. A third invention of the present invention relates to extrusion-molded articles and calender-molded articles obtained by respectively extrusion-molding or calendar-molding the above biodegradable resin composition.

[0007]

**[Practical Embodiment of the Invention]** Specific examples of  $C_3$  to  $C_{12}$   $\alpha$ -olefins of the present invention include propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, and 1-decene. If the  $\alpha$ -olefin has 13 or more carbon atoms, the costs of the  $\alpha$ -olefin monomers will increase, and industrial production becomes inconvenient. The  $C_3$  to  $C_{12}$

$\alpha$ -olefins may be used individually or in combinations of two or more. The  $\alpha$ -olefin content in the copolymer of the present invention must be 5 to 95% by weight, but is preferably 25 to 35% by weight when the  $\alpha$ -olefin has three to five carbons, and 25 to 40% by weight when the  $\alpha$ -olefin has 6 to 12 carbons. If the  $\alpha$ -olefin content is too low, the flexibility of the end product obtained using this copolymer will be poor. If the  $\alpha$ -olefin content is too high, the strength of the end product obtained using this copolymer will be poor.

[0008] The Mooney viscosity ( $M_{1+4}$  100°C) of the copolymer of the present invention must be 5 to 150, and preferably 20 to 80. If the Mooney viscosity is too low, bleeding will occur on the surface of the end product obtained using this copolymer. If the Mooney viscosity is too high, the workability of compositions obtained using this copolymer will deteriorate.

[0009] The tensile stress  $M_{100}$  of the copolymer of the present invention measured according to JIS-K-6251 must be 8 MPa or less, preferably 4 MPa or less, more preferably 2.5 MPa or less, and even more preferably 2.0 MPa or less. If this value is too high, the flexibility of the end product obtained using this copolymer will be poor.

[0010] The Q value (weight-average molecular chain length/number-average molecular chain length) of the copolymer of the present invention as measured by GPC must be four or higher, and preferably six or more. If the Q value is too small, the extrudability and calenderability of the composition obtained using the resulting copolymer will deteriorate. A higher Q value is preferred from the standpoint of extrudability and calenderability as long as the structural considerations of the present invention are fulfilled thereby. The Q value is measured by gel permeation chromatography (GPC; for example, using a 150C/GPC made by Waters Corporation). The elution temperature is 140°C, a Shodex Packed Column A-80M made by Showa Denko K.K. or the like is used as the column, and polystyrene (e.g. with a molecular weight of 68 to 8,400,000; manufactured by Tosoh Corporation) is used as the molecular weight reference substance. The resulting weight-average molecular weight ( $M_w$ ) and number-average molecular weight ( $M_n$ ) calculated for polystyrene, and the ratio therebetween (Q value), are taken to be the molecular weight distribution. Approximately five milligrams of polymer is dissolved in five milliliters of *o*-dichlorobenzene to create a measurement sample with a concentration of about 1 mg/mL. 400  $\mu$ L of the resulting sample is injected and eluted by a refractive index detector using an eluent flow rate of 1.0 mL/min.

[0011] The copolymer of the present invention is an ethylene- $\alpha$ -olefin copolymer that satisfies the above conditions (a) through (d), with an ethylene- $\alpha$ -olefin copolymer that also satisfies the following condition (e) being preferable.

(e) The molecular weight distribution curve must exhibit two or more peaks

[0012] Broadening of the molecular weight distribution will be inadequate if there is only one peak on the molecular weight distribution curve of the copolymer of the present invention, and there will be a deterioration in either the calenderability or the extrudability, and especially the texture of the extrusion surface, of articles molded from compositions in which the resulting copolymer has been used. The number of peaks in the molecular weight distribution curve of the copolymer of the present invention may be, e.g., two (bimodal), three (trimodal), and four (tetramodal).

[0013] The density of the copolymer of the present invention at 23°C is preferably 0.90 g/cm<sup>3</sup> or less, more preferably 0.89 g/cm<sup>3</sup> or less, even more preferably 0.88 g/cm<sup>3</sup> or less, and especially 0.87 g/cm<sup>3</sup> or less, in consideration of improving the flexibility of articles molded using the resulting biodegradable composition.

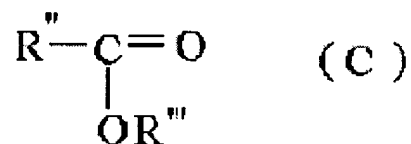
[0014] The copolymer of the present invention can be manufactured by polymerizing the ethylene and  $\alpha$ -olefin using one or two polymerization reactors in the presence of a catalyst system obtained by combining the following components (A) through (C) as described below. It is also possible to use three or more polymerization reactors as long as they meet the structural requirements of the present invention.

[0015] A vanadium compound shown by the general formula  $\text{VO}(\text{OR})_n\text{X}_{3-n}$  (where R is a hydrocarbon group, X is a halogen, and  $0 \leq n \leq 3$ ) can be used as component (A). Examples include  $\text{VOCl}_3$ ,  $\text{VO}(\text{OCH}_3)\text{Cl}_2$ ,  $\text{VO}(\text{OCH}_3)_2\text{Cl}$ ,  $\text{VO}(\text{OCH}_3)_3$ ,  $\text{VO}(\text{OC}_2\text{H}_5)\text{Cl}_2$ ,  $\text{VO}(\text{OC}_2\text{H}_5)_2\text{Cl}$ ,  $\text{VO}(\text{OC}_2\text{H}_5)_3$ ,  $\text{VO}(\text{OC}_3\text{H}_7)\text{Cl}_2$ ,  $\text{VO}(\text{OC}_3\text{H}_7)_2\text{Cl}$ ,  $\text{VO}(\text{OC}_3\text{H}_7)_3$ ,  $\text{VO}(\text{Oiso-C}_3\text{H}_7)\text{Cl}_2$ ,  $\text{VO}(\text{Oiso-C}_3\text{H}_7)_2\text{Cl}$ ,  $\text{VO}(\text{Oiso-C}_3\text{H}_7)_3$ ,  $\text{VO}(\text{On-C}_4\text{H}_9)\text{Cl}_2$ ,  $\text{VO}(\text{On-C}_4\text{H}_9)_2\text{Cl}$ , and  $\text{VO}(\text{On-C}_4\text{H}_9)_3$ , as well mixtures thereof. Compounds other than  $\text{VOCl}_3$  can be readily obtained by carrying out a reaction between  $\text{VOCl}_3$  and an alcohol, or between  $\text{VOCl}_3$  and  $\text{VO}(\text{OR})_3$ .

[0016] An organic aluminum compound shown by the general formula  $\text{R}'_m\text{AlX}_{3-m}$  (where, R' is a hydrocarbon group, X is a halogen, and  $0 \leq m \leq 3$ ) can be used as component (B). Examples include  $(\text{C}_2\text{H}_5)_2\text{AlCl}$ ,  $(\text{C}_4\text{H}_9)_2\text{AlCl}$ ,  $(\text{C}_6\text{H}_{13})_2\text{AlCl}$ ,  $(\text{C}_2\text{H}_5)_{1.5}\text{AlCl}_{1.5}$ ,  $(\text{C}_4\text{H}_9)_{1.5}\text{AlCl}_{1.5}$ ,  $(\text{C}_6\text{H}_{13})_{1.5}\text{AlCl}_{1.5}$ ,  $\text{C}_2\text{H}_5\text{AlCl}_2$ ,  $\text{C}_4\text{H}_9\text{AlCl}_2$ , and  $\text{C}_6\text{H}_{13}\text{AlCl}_2$ .

[0017] Although the copolymer of the present invention can also be obtained by using a catalyst system composed only of component (A) and component (B), component (C) shown below should be used in combination therewith to further reduce the number of low molecular-weight components that bleed out.

[0018] Halogenated ester compounds shown by the following general formula can be used as component (C).



(where R'' is a partially or completely halo-substituted C<sub>1</sub> to C<sub>20</sub> organic group and R''' is a C<sub>1</sub> to C<sub>20</sub> hydrocarbon group). All of the substituents of R'' are preferably chloro-substituted compounds, and more preferably perchlorocrotonic acid esters, which are especially effective. Concrete examples include ethyl dichloroacetate, methyl trichloroacetate, ethyl trichloroacetate, methyl dichlorophenyl acetate, ethyl dichlorophenyl acetate, methyl perchlorocrotonate, ethyl perchlorocrotonate, propyl perchlorocrotonate, isopropyl perchlorocrotonate, butyl perchlorocrotonate, cyclopropyl perchlorocrotonate, and phenyl perchlorocrotonate.

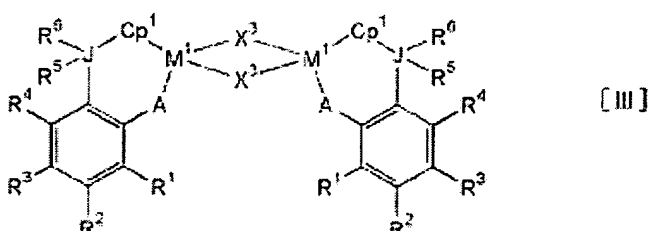
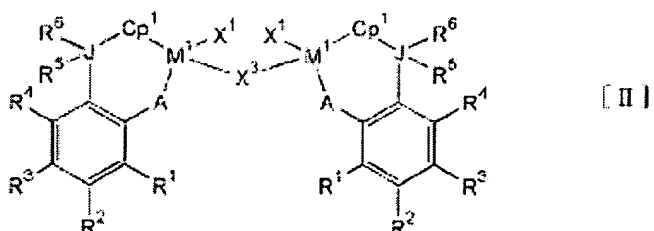
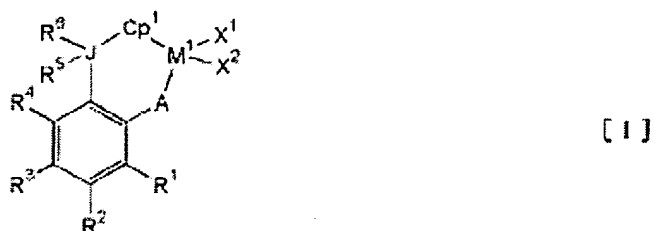
[0019] The ratio of the organic aluminum compound (B) and vanadium compound (A) in the polymerization reaction must be 2.5 or more in terms of the molar ratio and the ratio of the halogenated ester compound (C) and vanadium compound (A) must be 1.5 or more in terms of the molar ratio.

[0020] The copolymer of the present invention can also be manufactured using one or two or more polymerization reactors by using one or more known Ziegler-Natta catalysts or known single-site catalysts (such as metallocene catalysts) in addition to the above catalyst system. A known single-site catalyst (such as a metallocene catalyst) is preferred in consideration of the uniformity of the composition distribution of the resulting polymer. Examples of such single-site catalysts include the metallocene catalysts cited in Japanese Laid-Open Patent Application (Kokai) Nos. 58-19309, 60-35005, 60-35006, 60-35007, 60-35008, 61-130314, 3-163088, 4-268307, 9-12790, 9-87313, 10-508055, 11-80233, and 10-508055; and the non-metallocene complex catalysts cited in 10-316710, 11-100394, 11-80228, 11-80227, 10-338706, 11-71420, and Domestic Republication 10-513489. Among these, metallocene catalysts are commonly used. Examples of ideal metallocene catalysts among these have at least one cyclopentadiene-



type anion skeleton and, in terms of the flexibility of the resulting polymer, transition metal complexes from groups 3 through 12 of the periodic table that have a  $C_1$  symmetrical structure. An example of a suitable manufacturing method using a metallocene catalyst to obtain a high molecular-weight polymer involves copolymerizing ethylene and an  $\alpha$ -olefin in the presence of an olefin polymerization catalyst fabricated using ( $\alpha$ ) below and ( $\beta$ ) and/or ( $\gamma$ ) below

( $\alpha$ ) At least one of the transition metal complexes shown by general formulae [I] through [III] below:



(In the above general formulae [I] through [III],  $M_1$  is a transition metal atom of group 4 of the periodic table of the elements, A is an atom of group 16 of the periodic table, and J is an atom of group 14 of the periodic table.  $Cp_1$  is a group with a cyclopentadiene-type anion skeleton.  $X_1$ ,  $X_2$ ,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ , and  $R_6$  are each hydrogen atoms, halogen atoms, alkyl groups, aralkyl groups, aryl groups, substituted silyl groups, alkoxy groups, aralkyloxy groups, aryloxy groups, or bisubstituted amino groups.  $X_3$  is an atom of group 16 of the periodic table of the elements.  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ , and  $R_6$  may form rings by any type of bonding. Any two of  $M_1$ , A, J,  $Cp_1$ ,  $X_1$ ,  $X_2$ ,  $X_3$ ,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ , and  $R_6$  may be the same or different.)

( $\beta$ ) One or more aluminum compounds selected from among ( $\beta 1$ ) through ( $\beta 3$ ) below

(β1) Organic aluminum compounds shown by the general formula  $E_{1a}AlZ_{3-a}$

(β2) Cyclic aluminoxane with a structure shown by the general formula  $\{-Al(E_2)-O-\}_b$

(β3) Linear aluminoxane with a structure shown by the general formula  $E_3\{-Al(E_3)-O-cAlE_{32}$

(where,  $E_1$ ,  $E_2$ , and  $E_3$  are each hydrocarbon groups and all  $E_1$ , all  $E_2$ , and all  $E_3$  may be the same or different.  $Z$  is a hydrogen atom or halogen atom and all  $Z$  may be the same or different.  $A$  is a number that satisfies  $0 < a \leq 3$ ,  $b$  is an integer of 2 or more, and  $c$  is an integer of 1 or more.)

(γ) Any boron compound of (γ1) through (γ3) below

(γ1) Boron compounds shown by the general formula  $BQ_1Q_2Q_3$

(γ2) Boron compounds shown by the general formula  $G_+(BQ_1Q_2Q_3Q_4)-$

(γ3) Boron compounds shown by the general formula  $(L-H)_+(BQ_1Q_2Q_3Q_4)-$

(wherein  $B$  is a boron atom in a trivalent state of atomic valence,  $Q_1$  through  $Q_4$  are halogen atoms, hydrocarbon groups, halogenated hydrocarbon groups, substituted silyl groups, alkoxy groups, or bisubstituted amino groups; and these may be the same or different.  $G_+$  is an inorganic or organic cation,  $L$  is a neutral Lewis base, and  $(L-H)_+$  is a Bronsted acid.)

**[0021]** Specific examples of the inert hydrocarbon medium used in catalyst preparation include aliphatic hydrocarbons such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane, and kerosene; alicyclic hydrocarbons such as cyclopentane, cyclohexane, and methyl cyclopentane; aromatic hydrocarbons such as benzene, toluene, and xylene; halogenated hydrocarbons such as ethylene chloride, chlorobenzene, and dichloromethane; and mixtures of these. The preparation temperature preferably ranges from  $-100$  to  $250^\circ\text{C}$  and the pressure and time can be set as desired.

**[0022]** Polymerization of the copolymer of the present invention can be carried out in a hydrocarbon solvent. Examples of hydrocarbon solvents include aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, and kerosene; cyclic aliphatic hydrocarbons such as cyclohexane, methyl cyclopentane, and methyl cyclohexane; and aromatic hydrocarbons such as benzene, toluene, and xylene. An  $\alpha$ -olefin such as propylene, 1-butene, 1-pentene, or 1-hexene can also be used as part or all of the solvent. The polymerization temperature is preferably  $40$  to  $160^\circ\text{C}$  and more preferably  $40$  to  $80^\circ\text{C}$  in terms of productivity and molecular weight control.

[0023] Polymerization is conducted using one polymerization reactor or two polymerization reactors in series under atmospheric or increased pressure, preferably 0.1 to 5 MPa, and especially 0.1 to 2 MPa. The average residence time of the reaction solution per reactor is preferably 2 to 180 minutes, and more preferably 20 to 120 minutes. The polymer concentration is preferably 15% by weight or less, and more preferably 12% by weight or less, in consideration of lowering the viscosity of the reaction solution.

[0024] Hydrogen, diethylamine, aryl chloride pyridine-N-oxide, and the like may be used to control the molecular weight of the copolymer of the present invention. Hydrogen is especially preferred.

[0025] When two reactors are used, the temperature of the first and second polymerization reactors and the molecular weight regulator can be set as desired so as to satisfy the structural requirements of the present invention. However, a high molecular-weight polymer is preferably synthesized in the first reactor and a low molecular-weight polymer in the second reactor. The polymerization temperature of the first reactor is preferably 40 to 60°C and that of the second reactor is 50 to 80°C. If the polymerization temperature of the first reactor is too high, the molecular weight of the high molecular-weight polymer may become unsatisfactory. If the polymerization temperature of the second reactor is too low, a large amount of molecular weight regulator must be used, which is undesirable.

[0026] The molecular weight regulator can be added to either the first or second reactor, or to both, but preferably a satisfactory high molecular-weight polymer and low molecular-weight polymer can be polymerized by using a small amount in the first reactor and a large amount in the second reactor.

[0027] The ratio of the copolymer produced in the first and second reactors is preferably in a range of 2.0/0.05 to 1/2.5. Even better results are obtained in a range of 2.0/0.1 to 2/1.5.

[0028] Another method of synthesis that can be considered involves separately synthesizing a copolymer obtained by the above method and a copolymer that satisfies the same structural requirements, and blended them together.

[0029] However, the joint (hybrid) use of a known Ziegler-Natta catalyst or single-site catalyst as described above makes it possible to simultaneously polymerize and blend a high molecular-weight polymer and low molecular-weight polymer. This method is also suitable for mass

production. Furthermore, multiple polymerization reactors need not be used in this case, with even one reactor being adequate.

[0030] The copolymer of the present invention is preferably fashioned into pellets when used to modify polyolefin-based resins.

[0031] These copolymer pellets may be round, cylindrical, lens-shaped, cubic, or configured in another form. These can be manufactured by any known pelletizing method; e.g., round, cylindrical, and lens-shaped pellets can be obtained by uniformly melt-mixing the copolymer, extruding the resulting mixture with an extruder, and then hot-cutting or strand-cutting the extrudate. Cutting in this case can be performed in water or in a stream of air or another gas. Cubic pellets can be obtained, for example, by producing a uniform mixture, molding the mixture into the form of a sheet on rolls or the like, and using a sheet pelletizer. The length of the longest part of the pellet is preferably 3 cm or less. The measurement error may increase when larger-sized pellets are used.

[0032] The surfaces of these copolymer pellets are preferably covered with one or more types of pulverulent calcium stearate, calcium carbonate, barium sulfate, silica, talc, stearic acid, or polyolefin powder in order to prevent them from sticking to one another and to suppress bridging when the pellets are removed from silos or the like. The powder should be used in the requisite amount as dictated by the pellet size and shape. It is usually preferable to add 0.05 to 3 parts by weight relative to the copolymer pellets. If too little is added, the pellets cannot be prevented from sticking together. If too much is added, the characteristics will deteriorate, and production costs will increase. It is especially preferable to use polyolefin powder if importance is placed on the transparency of the end product. Examples of polyolefin powders include polyethylene-based resin and polypropylene-based resin powders.

[0033] The average particle diameter of the polyolefin powder is preferably 500  $\mu\text{m}$  or less, and especially 300  $\mu\text{m}$  or less. If the particle diameter is too large, the powder may not adhere to the pellet surface or prevent the pellets from sticking together.

[0034] Additives such as crystal nucleating agents, transparency promoters, heat stabilizers, ultraviolet stabilizers, weather stabilizers, foaming agents, antifogging agents, rust preventers, ion-trapping agents, flame retardants, flameproofing auxiliaries, inorganic fillers, organic pigments, inorganic pigments, and lubricants can be added as necessary during the manufacture of these copolymer pellets. Resins and rubbers such as polyethylene-based resins, ethylene-vinyl

acetate copolymers, ethylene-(meth)acrylic acid copolymers, ethylene-(meth)acrylate copolymers, saponified ethylene-vinyl acetate copolymers, ethylene-styrene copolymers, polypropylene-based resins, polybutene-1, petroleum resins, ethylene-propylene-unconjugated diene copolymer rubbers, polybutadiene, styrene-butadiene block copolymer rubbers, styrene-butadiene-styrene block copolymer rubbers, styrene-butadiene random copolymer rubbers, partially hydrogenated styrene-butadiene-styrene block copolymer rubbers, partially hydrogenated styrene-butadiene random copolymer rubbers, styrene-isoprene block copolymer rubbers; and partially hydrogenated styrene-isoprene block copolymer rubbers can also be added within a range that does not compromise the performance of the pellets.

[0035] The biodegradable resin composition derived from the novel ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins of the present invention shall be described hereunder. The biodegradable resin composition of the present invention is composed of (A) 5 to 95 parts by weight of the ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins of the present invention and (B) 5 to 95 parts by weight of a biodegradable resin, preferably 10 to 90 parts by weight of (A) and 10 to 90 parts by weight of (B), and more preferably 20 to 80 parts by weight of (A) and 20 to 80 parts by weight of (B). If too much of (A) (too little (B)) is used, the biodegradability the resulting biodegradable resin composition and the low heat generation during the incineration thereof will be poor. On the other hand, if too much of (B) (too little (A)) is used, the extrudability and calenderability of the biodegradable resin composition will not be improved to an adequate level.

[0036] Component (B) used in the biodegradable resin composition of the present invention is a biodegradable resin. (B) can be selected from among a wide range of a variety of known biodegradable resins. However, (B) preferably contains at least one or more types selected from among biodegradable resins based on starch, corn starch, microbes, succinic acid, polyester amides, polycaprolactones, cellulose acetates, and polylactic acid.

[0037] As deemed appropriate, additives such as antioxidants, antistatic agents, anti-weathering agents, UV absorbers, colorants, dispersants, and lubricants; colorants such as carbon black; fillers such as glass fibers, carbon fibers, metal fibers, aramid fibers, glass beads, asbestos, mica, calcium carbonate, potassium titanate whiskers, talc, barium sulfate, and glass flakes; other rubbery polymers; thermoplastic resins; and the like can also be compounded as additional components in addition to the above components in the present invention.

[0038] Waxes, higher alcohols, fatty acids, fatty acid metal salts, fatty acid amides, carboxylic acid esters, phosphoric acid esters, sulfonic acid metal salts, acid ester metal salts, acrylic resins, fluorine-containing resins, silicones, and the like can be used as lubricants. Two or more types may be used in combination.

[0039] Examples of waxes include petroleum waxes such as paraffin wax and microcrystalline wax, vegetable-based waxes such as rice wax, mineral-based waxes such as montan wax, and synthetic waxes such as polyethylene wax and low molecular-weight polypropylene.

[0040] Examples of higher alcohols include lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, behenyl alcohol, oleyl alcohol, erucyl alcohol, and 12-hydroxystearyl alcohol.

[0041] Examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, oleic acid, erucic acid, linoleic acid, and ricinoleic acid.

[0042] Examples of fatty acid metal salts include salts of metals such as Li, Na, Mg, Al, K, Ca, Zn, Ba, and Pb of fatty acids such as lauric acid, palmitic acid, stearic acid, behenic acid, oleic acid, erucic acid, linoleic acid, and ricinoleic acid. Specific examples include lithium stearate, sodium stearate, calcium stearate, and zinc stearate.

[0043] Examples of fatty acid amides include lauramide, palmitamide, stearamide, behenamide, oleamide, erucamide, methylenebis(stearamide), ethylenebis(stearamide), ethylenebis(oleamide), and stearyl diethanolamide.

[0044] Examples of carboxylic acid esters include esters of acrylic acid, crotonic acid, isocrotonic acid, fumaric acid, maleic acid, succinic acid, aconitic acid and other aliphatic carboxylic acids; lauric acid, palmitic acid, stearic acid, behenic acid, oleic acid, erucic acid, linoleic acid, ricinoleic acid, and other fatty acids; and lactic acid, malic acid, tartaric acid, citric acid, and other oxycarboxylic acids; and other carboxylic acids; and of myristyl alcohol, palmityl alcohol, stearyl alcohol, behenyl alcohol, 12-hydroxystearyl alcohol, and other aliphatic alcohols; benzyl alcohol,  $\beta$ -phenylethyl alcohol, phthalyl alcohol, and other aromatic alcohols; and glycerin, diglycerin, polyglycerin, sorbitan, sorbitol, propylene glycol, polypropylene glycol, polyethylene glycol, pentaerythritol, trimethylolpropane, and other polyhydric alcohols; and other alcohols. Specific examples include glycerin monooleate, glycerin dioleate, polyethylene glycol monostearate, and citric acid distearate.

**[0045]** Examples of phosphoric acid esters include monoalkyl esters, dialkyl esters, and trialkyl esters of phosphoric acid and higher alcohols. A specific example is AX-1 made by Asahi Denka Co., Ltd.

**[0046]** Examples of acrylic resins include polymers whose main units are acrylic acid; acrylic acid esters such as methyl acrylate, ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate; methacrylic acid; and methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, and 2-ethylhexyl methacrylate. Specific examples include Metablen made by Mitsubishi Rayon Co., Ltd. and Kane Ace made by Kanegafuchi Chemical Industry Co., Ltd.

**[0047]** Examples of sulfonic acid metal salts include sodium stearyl sulfonate, sodium lauryl sulfonate, sodium dodecylbenzenesulfonate, sodium dodecyl-naphthalenesulfonate, potassium stearyl sulfonate, potassium lauryl sulfonate, dibutyl sodium sulfosuccinate, di-2-ethylhexyl sodium sulfosuccinate, lauryl 2-sodium sulfosuccinate, and lauryl 2-sodium polyoxyethylene sulfosuccinate.

**[0048]** Examples of acid ester metal salts include sulfuric acid ester salts such as sodium lauryl sulfate and potassium lauryl sulfate, and phosphoric acid ester salts such as sodium lauryl phosphate and potassium lauryl phosphate.

**[0049]** Examples of fluororesins include fluoro-olefins such as tetrafluoroethylene, hexafluoropropylene, fluoroalkyl ethylene, and perfluoroalkyl vinyl ether; fluoroalkyl acrylates such as perfluoroalkylene acrylate and perfluorometaalkylene acrylate; and polymers whose main unit is a fluoromonomer such as fluoroalkyl methacrylate. Specific examples include polytetrafluoroethylene and perfluoro(polyoxypropylene ethyl ether).

**[0050]** Examples of silicones include polymers whose main unit is a siloxane derivative such as dimethyl siloxane, methyl phenyl siloxane, and diphenyl siloxane. Specific examples include polydimethyl siloxane and polymethyl phenyl siloxane.

**[0051]** Examples of other rubbery polymers and thermoplastic resins include polyethylene-based resins, ethylene-vinyl acetate copolymers, ethylene-(meth)acrylic acid copolymers, ethylene-(meth)acrylate copolymers, saponified ethylene-vinyl acetate copolymers, ethylene-styrene copolymers, polypropylene-based resins, polybutene-1, petroleum resins, ethylene-propylene-unconjugated diene copolymer rubbers, polybutadiene, styrene-butadiene block copolymer rubbers, styrene-butadiene-styrene block copolymer rubbers, styrene-butadiene random copolymer rubbers, partially hydrogenated styrene-butadiene-styrene block copolymer rubbers,

partially hydrogenated styrene-butadiene random copolymer rubbers, styrene-isoprene block copolymer rubbers, and partially hydrogenated styrene-isoprene block copolymer rubbers.

[0052] Among these, rubbery polymers and thermoplastic resins that contain polar groups are examples of other rubbery polymers and thermoplastic resins that are preferred for improving the compatibility between the copolymer of the present invention and the biodegradable resin. Examples include ethylene-vinyl acetate copolymers, ethylene-(meth)acrylic acid copolymers, ethylene-(meth)acrylate copolymers, saponified ethylene-vinyl acetate copolymers, ethylene-styrene copolymers, and petroleum resins.

[0053] In the biodegradable resin composition of the present invention, (A), (B), and other additional components may be kneaded using an ordinary kneading apparatus such as a rubber mill, Brabender mixer, Banbury mixer, pressurized kneader, or twin-screw extruder. The kneading apparatus may be either an open or a closed apparatus, but a sealed type in which inert gas substitution can be performed is preferred. The kneading temperature is a temperature at which all of the mixed constituent components will melt. It is usually 80 to 250°C, and preferably 100 to 240°C. The kneading time depends on the type of kneading apparatus and the types and amounts of the constituent components to be blended, and accordingly cannot be stated definitively. However, with a kneading apparatus such as a pressurized kneader or Banbury mixer, a time of approximately three to ten minutes is ordinarily employed. All of the constituent components may be kneaded at once in the kneading process, or multistage kneading may be used whereby some of the constituent components are mixed and the remaining constituent components are added and kneading is continued thereafter.

[0054] The biodegradable resin composition of the present invention is a particularly excellent material for use in extrusion molding. Extrusion-molded articles of different shapes can be obtained by melt extruding the composition from an extruder whose tip is furnished with a die in the product shape, and then cooling and cutting the extrudate. Extruded sheets and films can also be obtained by inflation processing and T-die casting.

[0055] The biodegradable resin composition of the present invention is also a particular excellent material for use in calender molding. Calendered articles can be obtained by a sheeting process, whereby a smooth sheet is continuously produced with high thickness precision; a doubling process, whereby sheets are continuously produced with high thickness precision and no pinholes involving the lamination of the same or different types of thermoplastic elastomer



compositions and thermoplastic resin compositions; a topping process, whereby a laminated composite of sheets such as fabric are continuously produced; a friction process, whereby a thermoplastic elastomer composition is imprinted on a fabric to improve the adhesiveness; or a profiling process, whereby a pattern that has been engraved on a roll is continuously embossed on the surface of a sheet.

**[0056]** Articles molded from the biodegradable resin composition of the present invention can be used in a variety of applications such as packaging materials (e.g., films, sheets, bottles, caps, trays, and can carriers), agricultural materials (e.g., agricultural films and bundling tape), domestic products (e.g., diaper baskets, shopping bags, and trash bags), toner and ink for copiers, containers for the transportation and storage of cosmetics, paints, and foodstuffs; and for hoses, tubes, gaskets, packing, mats, and labels.

**[0057]**

**[Working Examples]** The present invention is described in detail below with reference to working examples; however, the present invention shall not be construed to be limited to these examples.

[I] Manufacture and evaluation of component (A)

Measurements were performed as described hereunder.

(1) GPC measurement

A Model 150C made by Waters Corporation was used as the GPC apparatus, the elution temperature was 140°C, a Shodex Packed Column A-80M was used as a column, and polystyrene (e.g., made by Tosoh Corporation; molecular weight 68 to 8,400,000) was used as the molecular weight reference substance. The resulting weight-average molecular weight (Mw) and number-average molecular weight (Mn) calculated for polystyrene, and the ratio therebetween ( $Q \text{ value} = Mw/Mn$ ), were used for the molecular weight distribution. The measurement sample was approximately five milligrams of polymer dissolved in five milliliters of *o*-dichlorobenzene to bring the concentration to approximately 1 mg/mL. A quantity of 400  $\mu$ L of the resulting sample solution was injected and detected by a refractive index detector at an eluent flow rate of 1.0 mL/min.

(2) Tensile stress

A sample was press-molded at 150°C. After obtaining a two millimeter-thick sheet, the tensile stress  $M_{100}$  of the copolymer was measured in accordance with JIS-K-6251. The test piece was formed into the shape of a No. 3 dumbbell.

(3) Mooney viscosity

The Mooney viscosity of the copolymer,  $ML_{1+4}$  100°C, was measured in accordance with JIS-K-6300.

**[0058] Working Example 1 (Synthesis of component (A))**

A quantity of 62.8 kg/hour of hexane as the polymerization solvent, 5.90 kg/hour of ethylene, and 22.44 kg/hour of propylene were continuously supplied from the bottom of a 100 L stainless steel polymerization reactor equipped with a stirrer. A quantity of 2.22 g/hour of  $VO(Oiso-C_3H_7)_3$  and 7.79 g/hour of ethyl aluminum sesquichloride (EASC) as a catalyst were continuously supplied, and the temperature of the polymerization reactor was kept at 50°C. Part of the polymerization solution from the first reactor was removed, and the polymer was deposited by means of steam stripping. After drying, 600 ppm of Irganox 1076 (antioxidant made by Ciba Specialty Chemicals) was introduced, and ethylene-propylene copolymer pellets were obtained by cutting and granulating the mixture in water. A quantity of 4.6 kg/hour of copolymer was accordingly obtained. The molecular weight was regulated by hydrogen. The resulting ethylene-propylene copolymer pellets for modifying biodegradable resins had a propylene content of 27.6% by weight, a Mooney viscosity ( $ML_{1+4}$  100°C) of 40.9, a Q value according to GPC of 6.6, a tensile stress ( $M_{100}$ ) of 1.1 MPa, and indicated a bimodal molecular weight distribution curve.

**[0059]**

**[Effect of the Invention]** As explained above, the present invention provides an ethylene- $\alpha$ -olefin copolymer for modifying biodegradable resins that exhibits excellent flexibility, extrudability, and calenderability when blended with a biodegradable resin; and reduces damage to incinerator furnaces because the end product generates minimal heat when incinerated; a biodegradable resin composition thereof; and extrusion-molded articles and calender-molded articles obtained by respectively extrusion-molding and calendar-molding the biodegradable resin composition.

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